



Potassium formate as a secondary refrigerant

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The properties of aqueous fluid of potassium formate were studied theoretically and experimentally in order to find an improved secondary refrigerant for indirect refrigeration systems. The most important advantages compared to the traditional aqueous solutions of alcohols and glycols are good thermodynamic properties, low toxicity and non-flammability. A remarkable benefit is a reduced change of a laminar flow. Volumetric heat is lower, which brings about a higher rate of mass flow, if the temperature change of the fluid is maintained constant. However, because of the clearly lower values of viscosity, the pumping power demand is at same level. Good thermal conductivity promotes good heat transfer. © 1997 Elsevier Science Ltd and IIR.

(Keywords: heat carrier; chemical composition; physical property; viscosity; specific heat; toxicity; flammability)

Le formiate de potassium comme frigorigène secondaire

Dans le but de trouver un meilleur frigorigène secondaire pour les systèmes de froid indirect, on a fait l'étude théorique et expérimentale des propriétés d'une solution aqueuse de formiate de potassium. De bonnes propriétés thermodynamiques, une faible toxicité et l'inflammabilité sont ses principaux atouts par rapport aux solutions aqueuses traditionnelles d'alcools et de glycols. La facilité d'éviter l'écoulement laminaire est un avantage remarquable. Sa moindre chaleur volumétrique nécessite un débit massique supérieur pour une différence de température du fluide donnée. Cependant, en raison de sa viscosité nettement inférieure, la puissance au pompage reste au même niveau. Sa bonne conductivité thermique favorise un bon transfert de chaleur. © 1997 Elsevier Science Ltd et IIR.

(Mots clés: caloporteur; composition chimique; potassium; propriété physique; viscosité; chaleur massique; toxicité; inflammabilité)

Introduction

The requirement to minimize the use and release of harmful or hazardous refrigerants leads more and more to compact refrigeration packages. Properties of heat transfer fluids or secondary refrigerants, as they are often called, are essential for a reliable indirect refrigeration plant. Besides thermal and transport properties, other important properties are corrosivity, safety, toxicity, environmental characteristics and compatibility with common construction materials. This paper introduces a non-traditional substance, potassium formate (PF), and compares

its properties with some most frequently used aqueous fluids.

A number of papers on alternative secondary fluids have been published in the last few years (see e.g. Refs 1 and 2). Also some new fluids have been proposed, such as rape oil² as an environmentally friendly alternative for soil heat pump systems. The majority of traditional fluids are based on aqueous solutions of salts or some organic liquids, alcohols and glycols being the most common choices. Some non-aqueous liquids are used in low temperature applications.

None of the alternatives available can fulfil all the requirements for a good fluid. Aqueous salt solutions,

Nomenclature

| | |
|------------|-----------------------------------|
| A | Heat transfer area |
| c | Specific heat |
| d | Diameter |
| G | Thermal conductance |
| L | Length |
| \dot{m} | Mass flow rate |
| Nu | Nusselt number |
| P | Pumping power |
| Δp | Pressure loss |
| p | Pressure |
| Pr | Prandtl number |
| R | Thermal resistance |
| Re | Reynolds number |
| U | Overall heat transfer coefficient |
| w | Flow velocity |

| | |
|-----------|---------------------------|
| α | Heat transfer coefficient |
| λ | Thermal conductivity |
| Φ | Heat flow |
| η_p | Efficiency of the pump |
| ν | Kinematic viscosity |
| ρ | Density |
| ξ | Friction factor |

Subscripts

| | |
|---|---|
| 0 | Reference state |
| a | Secondary refrigerant in the air cooling coil |
| e | Secondary refrigerant in the evaporator |
| r | Secondary refrigerant |

like sodium chloride or potassium chloride, are very corrosive and a careful selection of inhibitors and materials is necessary. In practical installations, however, corrosion may proceed faster than expected and a frequent monitoring of the system is necessary.

The solutions of the most usual organic compounds have low thermal conductivity and high viscosity, especially at low temperatures. Therefore, their heat transfer is weak and the pressure loss is high, particularly at lower temperatures. One remarkable disadvantage is a risk of the laminar flow in the heat exchangers and therefore a dramatic drop in heat transfer. This poses a particular problem to shell and tube heat exchangers and plate finned air cooling heat exchangers. To increase the mixing of the flow, twisted tape inserts are often used in the tubes, but this causes further pressure loss. A plate type heat exchanger is not so sensitive because of a turbulence promoting form of the flow channels. Another reason is the low value of the critical Reynolds number, 100–400 compared to 2000–2500 in pipes. This transition from a turbulent flow to a laminar flow may be particularly problematic in cases where temperature is changing during the operation.

In the following, the main features of the aqueous solution of PF are described and some results of the comparisons with other organic aqueous solutions given. The aqueous mixtures to be compared are ethyl alcohol (EA), ethylene glycol (EG) and propylene glycol (PG).

Chemical nature

Potassium formate $HCOOK$ is a salt of formic acid. It can be prepared by absorbing carbon monoxide in 50–80% KOH at 100–200°C at a partial pressure of $CO > 690 \text{ kPa}$. The reaction is fairly slow³. The colourless and highly deliquescent crystals of PF have an orthorhombic symmetry and a density of 1910 kg m^{-3} . The crystals melt at 167°C and

decompose almost entirely to the oxalate at about 360°C with the evolution of H_2 .

Potassium formate is very soluble in water. The saturated aqueous solution at 18°C contains 76.8% PF by weight. Aqueous solution of PF may be readily manufactured from formic acid and KOH.

The corrosive properties of the solution are weak at the lower temperature levels. In aqueous solutions it is weakly alkaline and thus corrosion retarding. The corrosion can be prevented by proper inhibitors. Some traditional compounds are not soluble, examples of the suitable inhibitors are 1, 2, 4-triazole and borax.

The compatible elastomers are, for example, nitril rubber, chlorobutadiene rubber, chlorobutadiene rubber, polyvinylchloride, polyamide, polyethylene and aramides.

One remarkable advantage is it is environmentally friendly. Potassium formate is already widely in use in

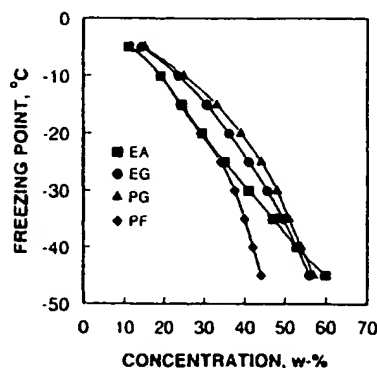


Figure 1 Freezing point temperature of fluids compared. EA, Ethyl alcohol; EG, ethylene glycol; PG, propylene glycol; PF, potassium formate

Figure 1 Températures des points de congélation de: EA, éthanol; EG, éthylène-glycol; PG, propylène-glycol; PF, formiate de potassium

the oil-drilling industry and as an ice removing agent for aeroplanes.

Thermodynamics properties

Figure 1 shows the freezing points of aqueous solutions of the fluids compared. The earlier values of freezing point data⁴ of PF solutions were verified with measurements in a cryogenic bath. It was found that the eutectic point may be even as low as -70°C with a saturated solution of PF. As seen in Figure 1 PF solutions generally have lower freezing points than the respective glycol solutions.

In the following, the fluids are compared with respect to their refrigerant properties at two different concentrations: the first concentration giving the freezing point -10°C and the second -25°C . The respective concentrations required for these freezing points are the following: 19 and 35% for EA, 23.5 and 41% for EG, 25 and 44% for PG, 19 and 35% for PF.

Volumetric specific heat for the solutions are presented in Figure 2. The specific heats of PF

solutions were estimated with a thermodynamic estimation program⁵. The specific heat was also measured with a reaction calorimeter (Mettler RC1) at two concentrations at various temperatures above room temperature. The agreement between the measured and the estimated values was good. As seen in Figure 2 the volumetric specific heat of PF is relatively low which means higher flow rates if a specified temperature change of the fluid has to be maintained.

Kinematic viscosity for the solutions as a function of temperature is plotted in Figure 3. The viscosities of PF solutions were measured with a capillary tube viscometer. Potassium formate has remarkably lower viscosities than the other fluids.

Methods of comparison of fluids

The comparison of secondary refrigerants cannot be based on one single property at a time, because several thermodynamic properties influence the performance. When studying the behaviour of the refrigeration system, a comparison can be applied:

- (a) to an existing system as a retrofit fluid; or
- (b) to a new system.

In the first case, the system components, like the pipes, the pump and the heat exchangers remain unaltered, only the secondary refrigerant and the mass flow are changed. This case may become indispensable if, for example, the rate of heat transfer of the old fluid is inadequately low.

In the second case, the whole system can be selected and dimensioned according to the requirements of the fluid. The dimensioning criteria can be based on different principles:

- (1) An optimization of the whole system using the total cost as the criterium. The sizes of the compressor, the air cooler and the size of the pipes should be included in the optimization. This is a rather complicated way and not very well defined or clear because of the great number of the parameters.
- (2) An optimization of the system using the total energy input (the compressor and the pump) as the criteria. When the mass flow rate of the secondary refrigerant is increased, the mean temperature of the fluid is increased and therefore the evaporation temperature, as well. Simultaneously, the energy supplied to the compressor is decreased and to the pump increased. Of course, the optimum is influenced by the relative amount of the pumping power. In this case, the dimensions of the pipes can be optimized separately using the total costs of the pipes as the criterium. According to earlier studies⁶, the optimum velocity is $0.5\text{--}1\text{ m s}^{-1}$. The total costs are rather insensitive to the velocity in the range given above.

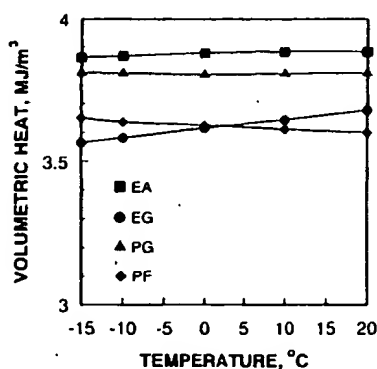


Figure 2 Volumetric specific heat for the solutions having the freezing point temperatures -10 and -25°C

Figure 2 Chaleur massique volumétrique pour des concentrations donnant des températures de point de congélation de -10 et -25°C

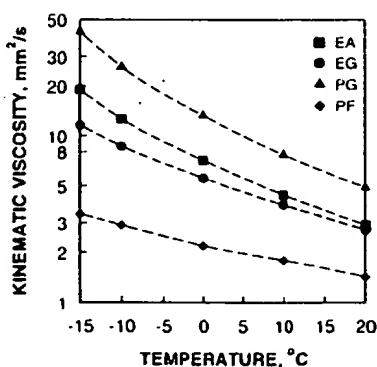


Figure 3 Kinematic viscosity of the solutions

Figure 3 Viscosité cinématique des solutions

Simple comparison of thermodynamic performance

The relevant thermodynamic properties can be combined in different ways in order to describe a particular performance. For example, the pressure drop or heat transfer properties can be compared separately, as done by Granryd and Melinder². However, pressure loss and heat transfer are inter-related in the heat exchangers, because an increased flow rate gives a better heat transfer with smaller temperature differences across the boundary layer.

One way to compare the pressure loss and the heat transfer simultaneously is to look at the pumping power, which is required to give a specified temperature difference between the fluid and the heat transfer surface. In order to obtain a simple approximate formula for illustration purposes, we can use the Blasius correlation for the friction factor and the Dittus-Boelter correlation for the heat transfer (in pipes) in the turbulent flow region:

$$\xi = C_f \text{Re}^{-0.2}$$

$$\text{Nu} = C_{\text{Nu}} \text{Re}^{0.8} \text{Pr}^{0.4} \quad (1)$$

From the equations above, we obtain the pumping power per pipe length:

$$P/L = C_{\text{Pl}} F_{\text{P}} \alpha^{2.25} d^{-0.75} \quad (2)$$

where C_{Pl} is a constant coefficient depending only on C_f and C_{Nu} . F_{P} is a property coefficient:

$$F_{\text{P}} = \nu^2 \rho \lambda^{-2.25} \text{Pr}^{-0.9} \quad (3)$$

In the similar way, for the laminar region we obtain

$$P/L = C_{\text{Pl}} F_{\text{P}} \alpha d^{-1} \quad (4)$$

If the temperature difference between the wall and the fluid, as well as the heat flux are constant, the heat transfer coefficient α is constant. In this way the property coefficient F_{P} indicates the differences in pumping power demand between the fluids, as shown for turbulent flow in Figure 4. In the laminar region, the differences are indicated directly by the dynamic

viscosity [Equation (4)], but usually the laminar case should be avoided and is therefore of minor interest.

Properties in a brine loop

One alternative method of the comparison is some kind of simulation of a whole secondary refrigerant loop. The influence of the fluid properties can be found out by applying a simple approach. A more sophisticated way is not needed to show the major differences between the fluids. An elementary modelling was carried out for the case of a simple loop shown in Figure 5. The comparisons were based on a reference state denoted by subscript 0. The reference fluid selected is propylene glycol, the reference state is specified in the Appendix. The calculations are based on the simple correlations and formulae shown below.

- (1) Heat transfer in the tubes of the evaporator and air cooling coil, Dittus-Boelter correlation according to Equation (1)
- (2) Pumping power

$$P = \dot{m}_f \Delta p / (\rho_f \eta_p) \quad (5)$$

where the efficiency η_p was assumed to be constant (0.7)

- (3) Heat flow in the heat exchangers

$$\Phi = G \frac{\Delta T_1 \Delta T_2}{\ln(\Delta T_1 / \Delta T_2)} \quad (6)$$

where ΔT_1 and ΔT_2 are the temperature differences at both ends of the heat exchanger and G is the thermal conductance ($= AU$, where U is the overall heat transfer coefficient).

The heat transfer coefficients on the air side and on the refrigerant side were kept constant. The change of the heat transfer coefficient in the air cooling coil compared to the reference state is calculated using Equation (1):

$$\alpha_a = \alpha_{a0} \left(\frac{\lambda_r}{\lambda_{r0}} \right)^{0.6} \left(\frac{\nu_r}{\nu_{r0}} \right)^{-0.2} \left(\frac{c_r}{c_{r0}} \right)^{0.4} \left(\frac{\rho_r}{\rho_{r0}} \right)^{0.6} \left(\frac{\dot{m}_r}{\dot{m}_{r0}} \right)^{0.4} \quad (7)$$

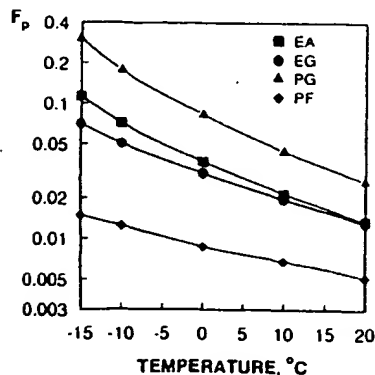


Figure 4 The property factor F_{P} in Equation (2)

Figure 4 Facteur F_{P} de l'Equation (2)

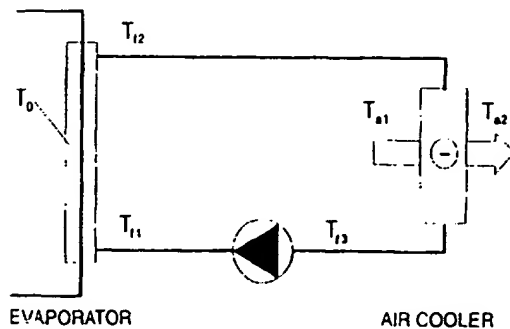


Figure 5 The simple cooling loop simulated

Figure 5 Simulation de la boucle de refroidissement simple

For the heat transfer rate in the coil three formulae can be written:

Air side:

$$\Phi_a = \dot{m}_a c_{pa} (T_{a1} - T_{a2}) \quad (8)$$

Liquid side:

$$\Phi_a = \dot{m}_r c_l (T_{r3} - T_{r2}) \quad (9)$$

Between the flows:

$$\Phi_a = G_a \frac{T_{a1} - T_{r3} - T_{a2} + T_{r2}}{\ln \frac{T_{a1} - T_{r3}}{T_{a2} - T_{r2}}} \quad (10)$$

Where the thermal conductance is:

$$G_a = A_a / (R_a + 1/\alpha_{ra}) \quad (11)$$

R_a is the thermal resistance in the brine side from the wall to air.

Similar equations can be written for the evaporator:

$$\alpha_{ac} = \alpha_{rc0} \left(\frac{\lambda_r}{\lambda_{r0}} \right)^{0.6} \left(\frac{\nu_r}{\nu_{r0}} \right)^{-0.2} \left(\frac{c_r}{c_{r0}} \right)^{0.4} \left(\frac{\rho_r}{\rho_{r0}} \right)^{0.6} \left(\frac{\dot{m}_r}{\dot{m}_{r0}} \right)^{0.4} \quad (12)$$

$$\Phi_c = \dot{m}_r c_l (T_{r1} - T_{r2}) \quad (13)$$

$$\Phi_c = G_c \frac{T_{r1} - T_{r2}}{\ln \frac{T_{r1} - T_c}{T_{r2} - T_c}} \quad (14)$$

$$G_c = A_c / (R_c + 1/\alpha_{rc}) \quad (15)$$

The change of pumping power in regard to the reference state can be based on Equations (1) and (5):

$$P = P_0 \left(\frac{\dot{m}_r}{\dot{m}_{r0}} \right)^{2.8} \left(\frac{\nu_r}{\nu_{r0}} \right)^{0.2} \left(\frac{\rho_r}{\rho_{r0}} \right)^{-1.8} \quad (16)$$

Only the pressure loss due to friction in the pipes is

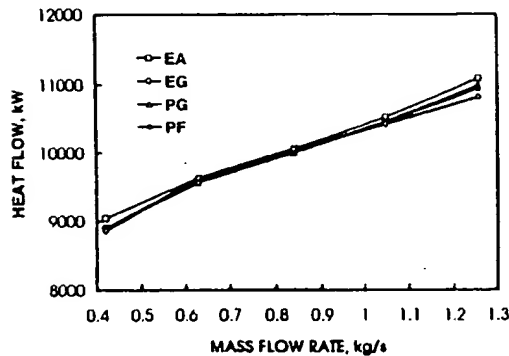


Figure 6 Calculated capacity of the evaporator. The freezing point temperature is -10°C and the mean temperature -2 to -3°C

Figure 6 Puissance calculée à l'évaporateur. La température du point de congélation est de -10°C et la température moyenne de -2 à -3°C

taken into the count in Equation (16). The fluid temperature increases in the pump (heat flow to the loop is omitted):

$$T_{r1} = T_{r3} + \frac{P}{c_l \dot{m}_r} \quad (17)$$

The known input parameters are the evaporation temperature T_c , the mass flow rate of fluid \dot{m}_r , the air inlet temperature T_{a1} , the mass flow rate of air \dot{m}_a . The surface areas A_a and A_c can be calculated from the reference state values. The refrigerant and air side heat transfer coefficients are assumed to be constant. The Equations (7) were solved using the standard Newton-Raphson iteration.

Sample results for turbulent flow are shown in Figures 6 and 7. Figure 6 shows the capacity of the evaporator vs the mass flow rate. Figure 7 shows the changes of the pumping power. At a specified mass flow rate, the refrigerant does not have a very great influence on the capacity of the evaporator. Better heat transfer of PF is compensated by the lower specific heat, which gives a higher temperature change

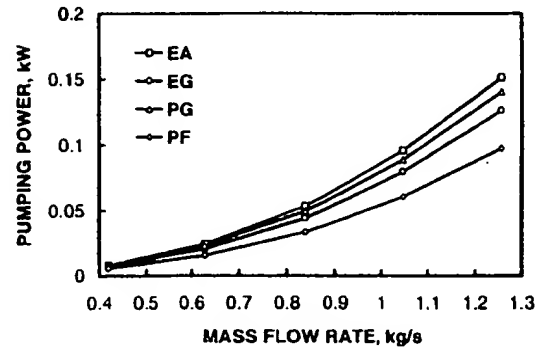


Figure 7 Calculated pumping power demand for the cases of Figure 6

Figure 7 Demande de puissance de pompage calculée pour les cas présentés dans la Figure 6

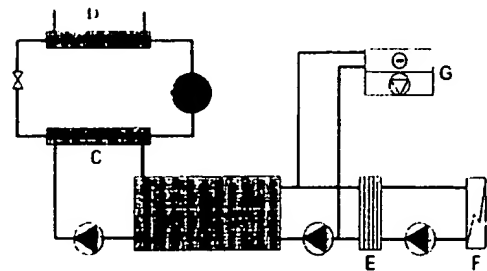


Figure 8 Schematic of the experimental set-up. A, Storage tank; C, evaporator; D, condenser; E, plate heat exchanger; F, electric heater; G, plate finned air cooling coil

Figure 8 Schéma du dispositif expérimental. A, Réservoir de stockage; C, évaporateur; D, condenseur; E, échangeur de chaleur à plaques; F, chauffage électrique; G, serpentin de refroidissement d'air à plaques-ailettes

of the refrigerant. However, if the mass flow rate is chosen to get the same pumping power, a higher capacity of the evaporator is obtained for PF. For fluid mixtures having a lower freezing temperatures, the improvement is even more pronounced.

Experimental comparisons

Experiments were carried out in a test rig illustrated in Figure 8. The liquid-liquid heat exchanger was a standard plate type. The flow rate in both sides were adjusted at the same value in order to determine the heat transfer coefficient between plates and fluid. The air cooler was a plate fin heat exchanger having 5 mm fin spacing, 0.25 mm fin thickness, 14.5/13.5 mm

copper tubes with 36/30 mm staggered spacing. The air flow rate was maintained constant.

From the measured temperatures, flow rates and pressures, pumping power demand and thermal conductance at various flow rates were determined. Some examples of the results are shown in Figures 9 and 10. The temperature of the secondary refrigerant in the figures is -5 to 3°C .

Figure 9 shows the thermal conductance, the temperature change and the pumping power for the plate heat exchanger when the freezing temperature is -10°C and the mean temperature -4°C . The thermal conductance G is defined by Equation (10).

Figures 9 and 10 enable comparisons of the performance results in different ways. One way is to compare heat transfer and conductance values at the same pumping power as above in theoretical studies. For example, if we take the value 20 for the pumping power, from Figure 10 the mass flow rate about 0.62 is obtained for EA and PG, 0.65 for EG and 0.72 for PF. Using these flow rates, the conductances are obtained using Figure 9. The conductance value is the lowest for PG. EA and EG give about 5% higher and PF about 60% higher conductances. In practice, the improvement is smaller because the secondary refrigerant flows only in one side of the heat exchanger. However, also in this case PF clearly improves heat transfer.

Similar but smaller improvements were observed in the air cooling coil. This is due to low heat transfer at the air side and thus the weaker influence of the secondary refrigerant on the total resistance. In practice, often more important is the possibility to avoid the laminar flow in the tubes of the coil.

Summary and conclusions

The properties of the non-traditional secondary

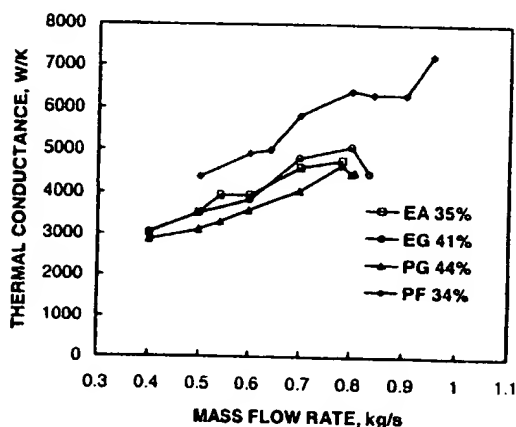


Figure 9 Measured thermal conductance of a plate heat exchanger. The freezing point temperature is -10°C .

Figure 9 Conductance thermique mesurée d'un échangeur de chaleur à plaques. La température du point de congélation est de -10°C .

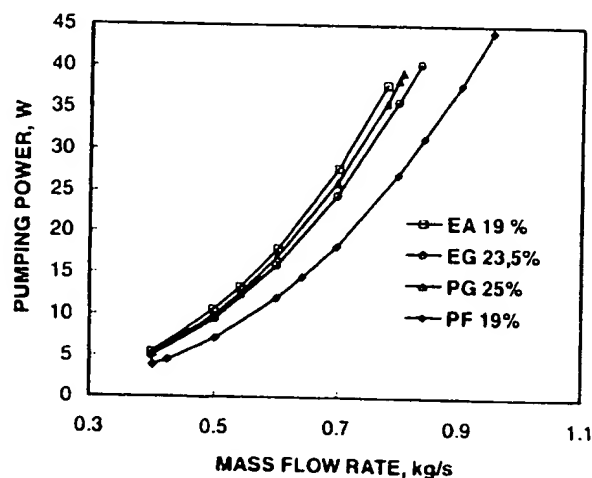


Figure 10 Measured pumping power demand. The freezing temperature is -10°C .

Figure 10 Demande de puissance de pompage mesurée. La température de congélation est de -10°C .

refrigerant, PF, were studied theoretically and experimentally. The most important advantages compared to the traditional aqueous solutions of alcohols and glycols are good thermodynamic properties, a low toxicity and non-flammability. Volumetric heat is lower, which requires a higher rate of mass flow, if the temperature change of the fluid is maintained constant. However, because of clearly lower values of viscosity, the pumping power demand is at same level. Also, good thermal conductivity promotes good heat transfer.

According to the results of theoretical and experimental comparisons, higher values of the thermal conductance of heat exchangers are achieved. One important feature in many cases is the possibility to avoid the laminar flow region in heat exchangers at lower velocities.

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Appendix: the reference state

$$T_{a1,0} = 5^{\circ}\text{C}$$

$$T_{a2,0} = 0^{\circ}\text{C}$$

$$T_{e0} = -5^{\circ}\text{C}$$

$$\dot{m}_{a0} = 0.25 \text{ kg s}^{-1}$$

$$\dot{m}_{r0} = 0.088 \text{ kg s}^{-1}$$

$$\alpha_{a0} = 20 \text{ W km}^{-2}$$

$$\alpha_{r0} = 500 \text{ W km}^{-2}$$

$$R_a = 0.05 \text{ km}^2 \text{ W}^{-1}$$

$$R_r = 0.002 \text{ km}^2 \text{ W}^{-1}$$